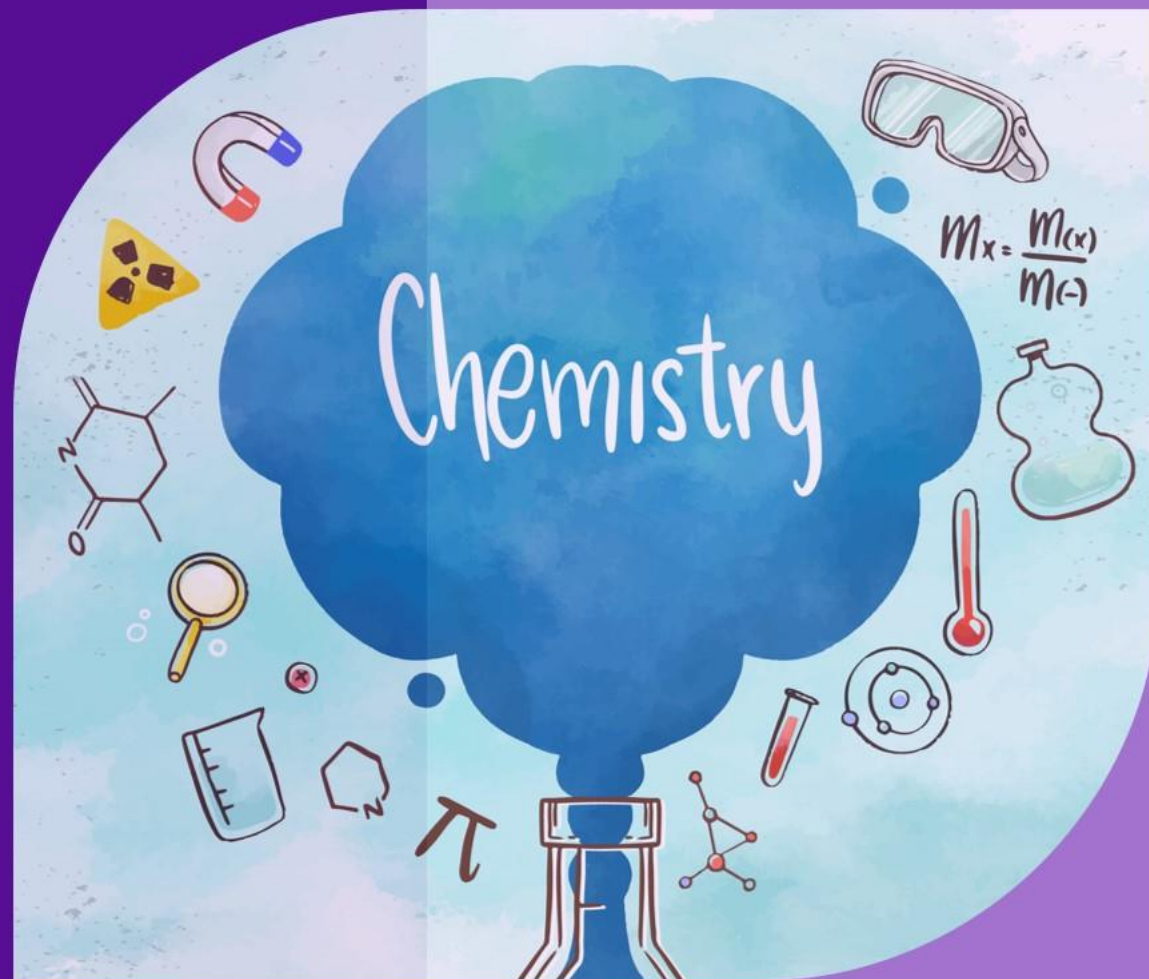


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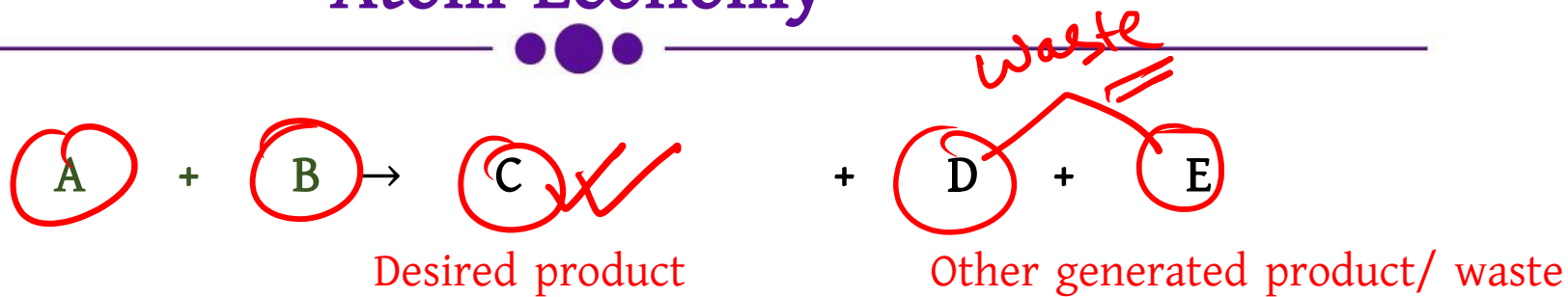
# CHEMISTRY

LECTURE : C-04

CHAPTER 04 : CHEMICAL EQUILIBRIUM

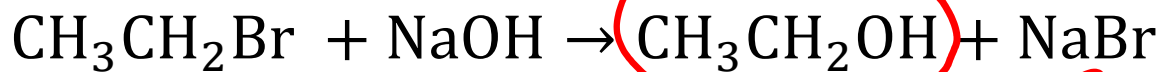


# Atom Economy



$$\% \text{ AE} = \frac{\textcircled{C}}{\textcircled{C} + \textcircled{D} + \textcircled{E}} \times 100$$

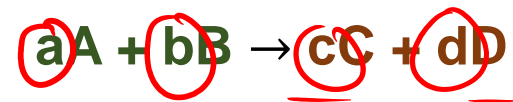
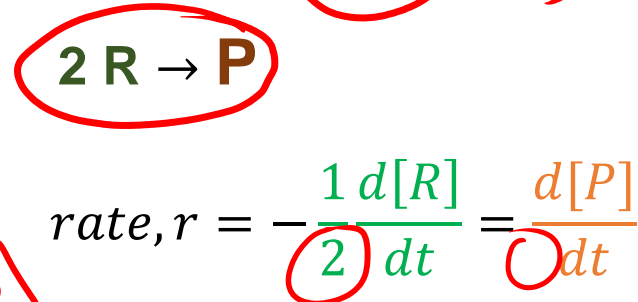
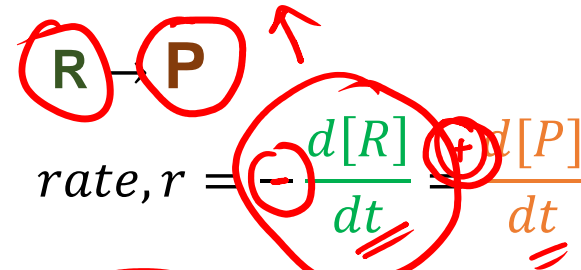
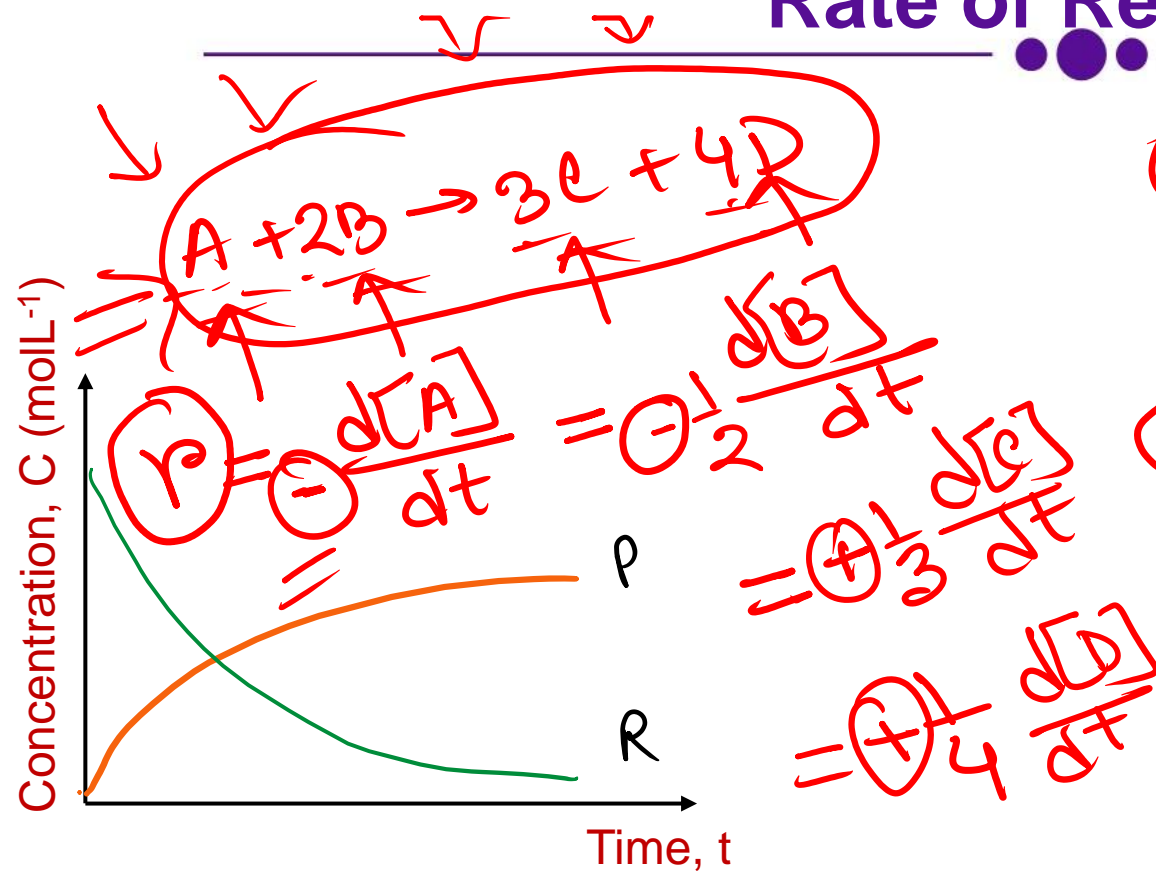
*desired product*



$$\% \text{ AE} = \frac{\text{mass of a}}{\text{mass of (a+b)}} \times 100\%$$

*a*      *b*

# Rate of Reaction



rate,  $r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$

$\text{'C' as rate} = \frac{d[C]}{dt}$

reaction rate w.r.t 'C'

$= \frac{1}{3} \frac{d[C]}{dt}$

## Problem-1

Ammonia reacts with oxygen by the given reaction-

$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$  at any instant, rate of reaction of ammonia is  $0.24 \text{ mol L}^{-1} \text{ s}^{-1}$

(a) Write the rate expression for the reaction

(b) Calculate rate of generation of water.

[BUET' 17-18]

$$\therefore \frac{d[\text{NH}_3]}{dt} = 0.24 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(a) \quad r = -\frac{1}{4} \cdot \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = +\frac{1}{4} \frac{d[\text{NO}]}{dt} = +\frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

$$(b) \quad \frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} = r$$

$$\therefore \frac{d[\text{H}_2\text{O}]}{dt} = \frac{6}{4} \frac{d[\text{NH}_3]}{dt} = \frac{6}{4} \times 0.24 = 0.36 \text{ mol L}^{-1} \text{ s}^{-1}$$

# Factors affecting reaction rate

order

1. Concentration



2. Pressure



3. Surface area of reactant



4. Temperature

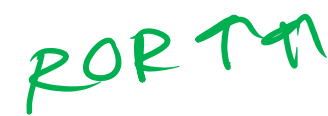
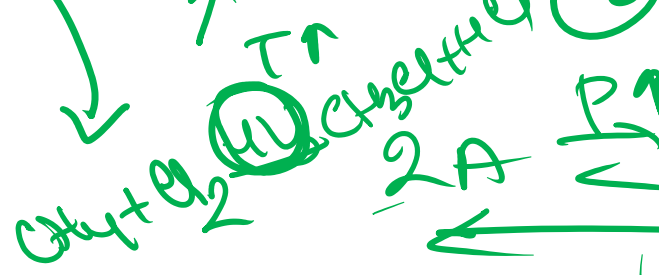


5. Catalyst



6. Nature of reactant

7. Presence of light



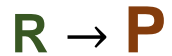
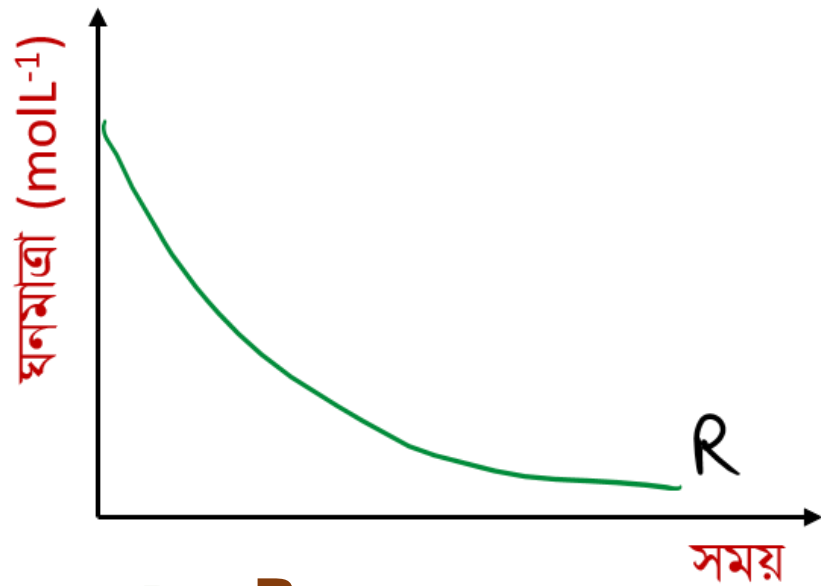
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Chemistry 1<sup>st</sup> Paper

Chapter 04 : Chemical Equilibrium

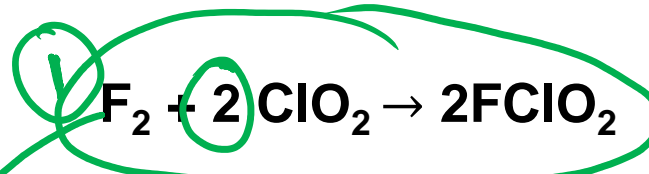
# Effect of Concentration; Order of Reaction:



$$r = f([R])$$

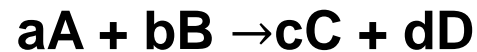
$$r \propto [R]^x = \text{order}$$

$$r = k[R]^x$$



[F <sub>2</sub> ]/M	[ClO <sub>2</sub> ]/M	Initial Rate, r/Ms <sup>-1</sup>
0.1	0.01	1.2x10 <sup>-3</sup>
0.1	0.04	4.8x10 <sup>-3</sup>
0.2	0.01	2.4x10 <sup>-3</sup>

$$r = k[F_2][ClO_2]^2$$



$$r = k (M^{1-(x+y)}s^{-1}) [A]^x [B]^y$$

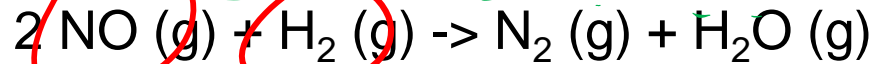
$$r = k[F_2]^x [ClO_2]^y$$

$$[k, x, y] \rightarrow \text{Order}$$

$$n = x + y$$

## Problem-2

Nitric oxide reacts with hydrogen gas to produce nitrogen and water vapor at 1280°C-



Data obtained from conducted experiments on this reaction are tabulated as follows. From this data-

- (a) Calculate rate law of the reaction  $\Rightarrow \textcircled{a} \text{ } r = k [\text{NO}]^x [\text{H}_2]^y$
- (b) Calculate the rate constant, k.
- (c) Calculate rate of this reaction when  $[\text{NO}] = 12 \times 10^{-3} \text{ M}$  and  $[\text{H}_2] = 6 \times 10^{-3} \text{ M}$

experimental  
value

[NO]/M	[H <sub>2</sub> ]/M	Initial Rate/Ms <sup>-1</sup>
5.0 × 10 <sup>-3</sup>	2.0 × 10 <sup>-3</sup>	1.3 × 10 <sup>-5</sup>
10.0 × 10 <sup>-3</sup>	2.0 × 10 <sup>-3</sup>	5.0 × 10 <sup>-5</sup>
10.0 × 10 <sup>-3</sup>	4.0 × 10 <sup>-3</sup>	10.0 × 10 <sup>-5</sup>

(b)  $1.3 \times 10^{-5} = k [5 \times 10^{-3}]^x [2 \times 10^{-3}]^y \quad \text{--- (i)}$

$5 \times 10^{-5} = k [10 \times 10^{-3}]^x [2 \times 10^{-3}]^y \quad \text{--- (ii)}$

$10 \times 10^{-5} = k [4 \times 10^{-3}]^y [10 \times 10^{-3}]^x \quad \text{--- (iii)}$

$x = 2$   
 $y = 1$

$k =$

## Problem-2 (Continued)...

$$x=2, y=1, K = \boxed{\text{Ans}}$$

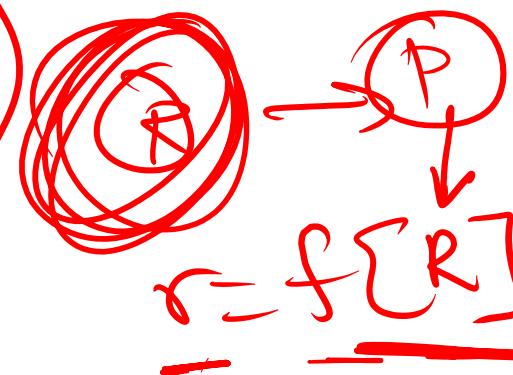
$$r = K [\text{NO}]^x [\text{H}_2]^y$$

order = x+y = 3

$$[\text{NO}] = 12 \times 10^{-3} \text{ M}, [\text{H}_2] = 6 \times 10^{-3} \text{ M}$$

$$\therefore \textcircled{r} = K [\text{NO}]^2 [\text{H}_2]^1$$

$K = \text{we know}$



$$r = \underline{\underline{f[R]}}$$

# Order of Reaction: 0<sup>th</sup> Order Reaction

A → products

$$-\frac{d[A]}{dt} = k_0 [A]^0$$

When,

$$t = 0, [A] = [A]_0$$

$$t = t, [A] = [A]_t$$

$$\Rightarrow -\frac{d[A]}{dt} = k_0 \cdot 1$$

$$\Rightarrow \int_{[A]_0}^{[A]_t} d[A] = -k_0 \int_0^t dt$$

$[A]_t/M$



When,

$$t = t_{1/2}, [A]_t = [A]_0/2$$

For 0<sup>th</sup> order reaction,

$$\frac{[A]_0}{2} = [A]_0 - k_0 t_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{2k_0}$$

half life  $t_{1/2} = 10$  molecule

$$t_{1/2} = 5$$

n = order

$$k = (\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$$



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Chemistry 1<sup>st</sup> Paper

Chapter 04 : Chemical Equilibrium

# Order of Reaction: 1st Order Reaction

$A \rightarrow \text{products}$

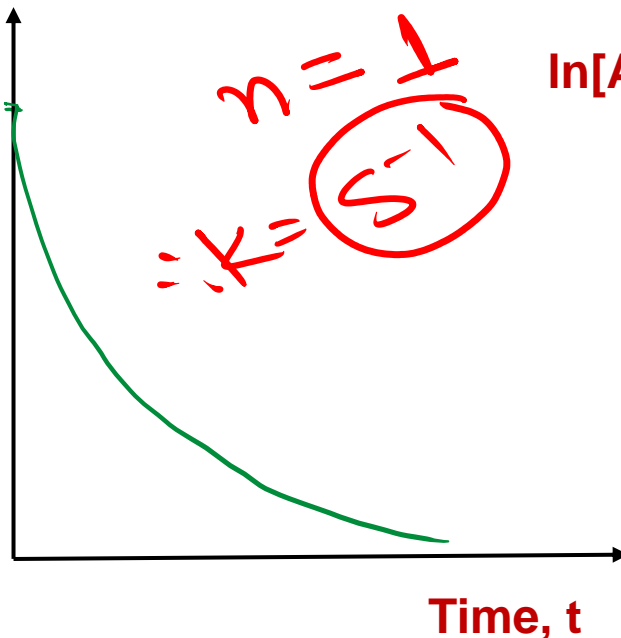
$$-\frac{d[A]}{dt} = k_1 [A]^1$$

When,

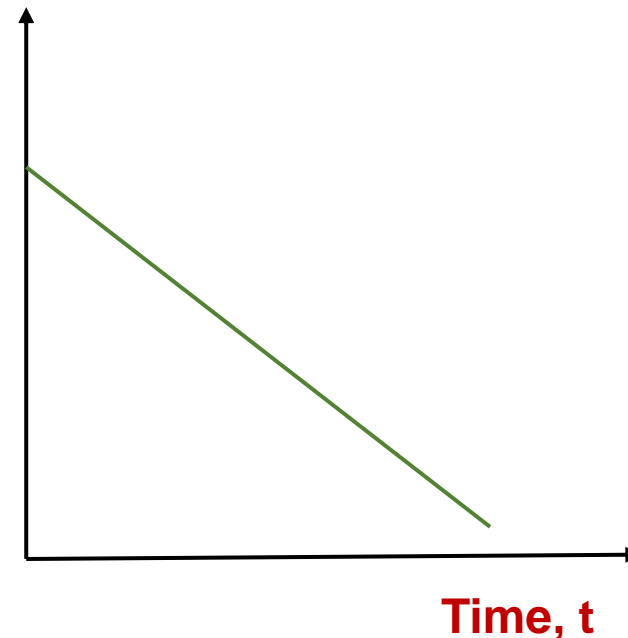
$$t = 0, [A] = [A]_0$$

$$t = t, [A] = [A]_t$$

$[A]_t/M$



$\ln[A]$



$$-\frac{d[A]}{dt} = k_1 [A]$$

$$\frac{d[A]}{[A]} = -k_1 dt$$

$$\ln \frac{[A]_t}{[A]_0} = -k_1 t$$

$$[A]_t = [A]_0 e^{-k_1 t}$$

$$\ln[A]_t = \ln[A]_0 - k_1 t$$



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# Half life of reaction, $t_{1/2}$

Time required for a single reactant reaction to completely convert its 50% reactant into product(s).

**A → products**

$$t_{1/2} = \frac{\ln 2}{k_1}$$

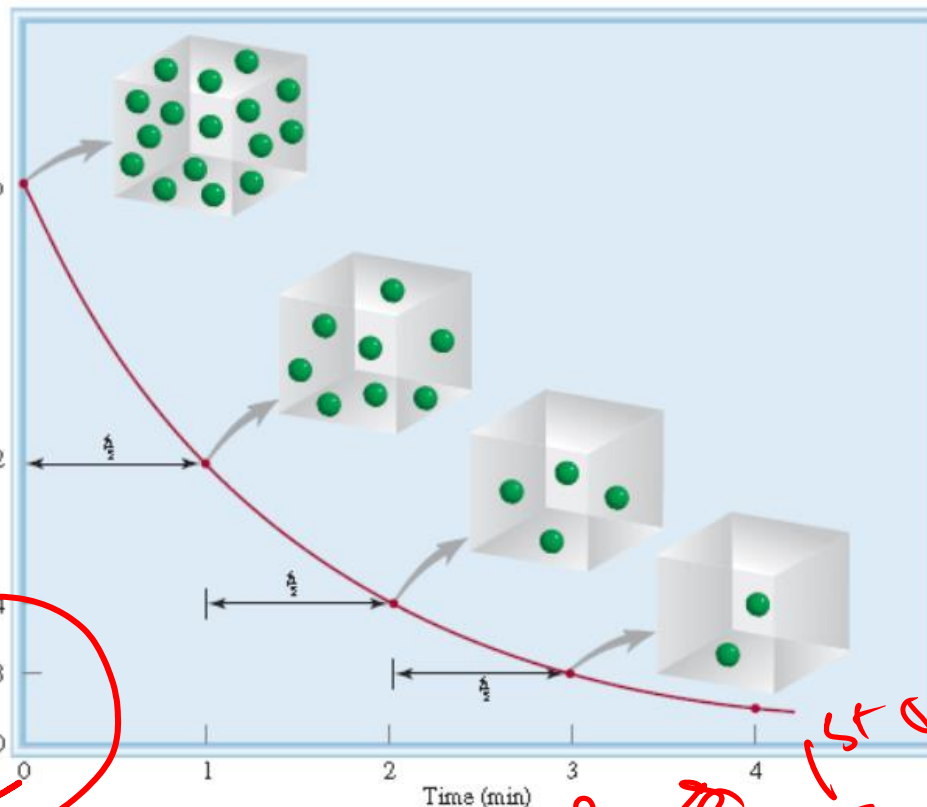
When,

$$t = t_{1/2}, [A]_t = [A]_0/2$$

For 1<sup>st</sup> order reaction,

$$\ln \frac{[A]_t}{[A]_0} = -k_1 t$$

$$\ln \frac{[A]_0}{2} = -k_1 t_{1/2}$$



## Problem-3

Rate constant for conversion of cyclopropane to propene is  $6.7 \times 10^{-4} \text{ s}^{-1}$ .

(a) What will be the concentration of cyclopropane after 8.8 minutes if its initial concentration was 0.25 M?

(b) What time will be required to reduce the concentration of cyclopropane from 0.25 M to 0.15 M?

$$t = (8.8 \times 60) \text{ sec}$$

$$[A]_t = [A]_0 e^{-kt} = \boxed{\phantom{0.15}} \text{ (Ans)}$$

remaining concentration =  $[A]_t = 0.15 \text{ M}$

$$[A]_t = [A]_0 e^{-kt}$$

$\downarrow \quad \quad \downarrow \quad \quad \downarrow$   
 $0.15 \quad \quad 0.25 \quad \quad 6.7 \times 10^{-4}$

$$\therefore t = \boxed{\phantom{0.15}}$$

BUET' 17-18

## Problem-4

A one reactant system takes 40 min to convert  $\frac{1}{5}$  of its reactant to product

order = 1

(a) Calculate  $t_{1/2}$  (min) of this conversion.

(b) What is the time required for 60% completion of the reaction?

(c) Calculate the time after which only 20% reactant will remain in the reaction vessel.

↑  
answer  
in  
min

$[A]_t = \frac{4}{5}[A]_0$        $t = (40 \times 60) \text{ s}$

order = 1:       $t_{1/2} = \frac{0.693}{k}$       ← Ans

$[A]_t = [A]_0 e^{-kt}$

$\frac{4}{5}A_0 = A_0 e^{-k(40 \times 60)}$

$\frac{4}{5}A_0 = A_0 e^{-k(40 \times 60)}$

$k = \frac{1}{24}$

## Problem-4 (Continued)...

⑥ 60% complete.

$$A_t = \frac{40}{100} \cdot A_0$$

$$k = \boxed{\phantom{000}} \text{ from (a)}$$

$$t = ? = \boxed{\phantom{000}}$$

⑦

$$A_t = \frac{20}{100} \times A_0$$

$$k = \text{from (a)}$$

$$\therefore t = \boxed{\phantom{000}}$$

# Order of Reaction: 2nd Order Reaction

$A \rightarrow \text{products}$

$$-\frac{d[A]}{dt} = k_2 [A]^2$$

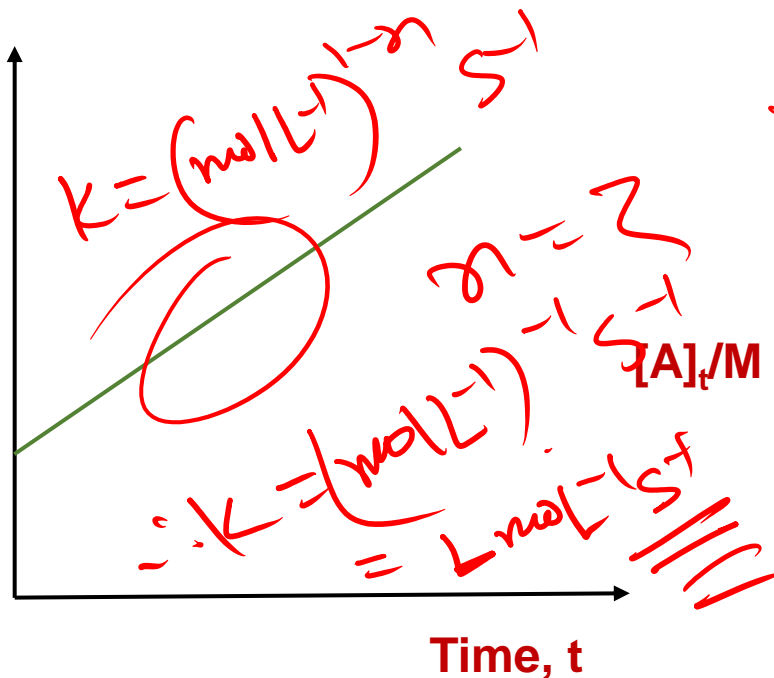
When,

$$t = 0, [A] = [A]_0$$

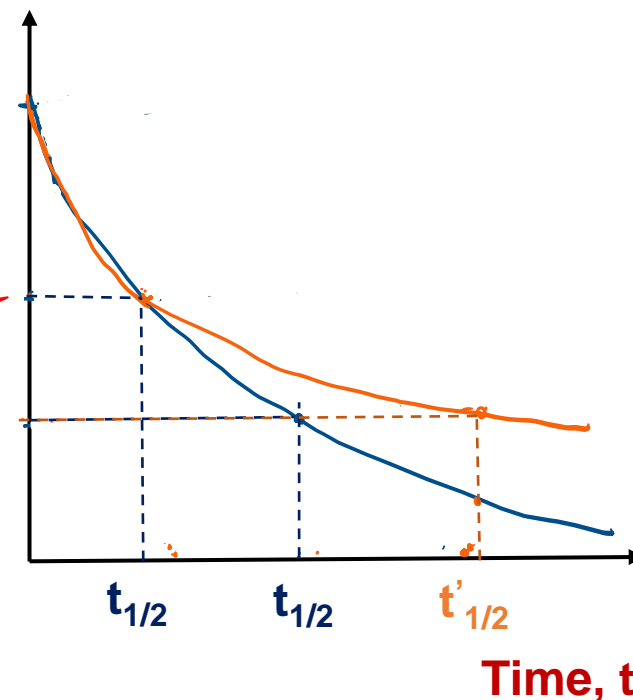
$$t = t, [A] = [A]_t$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t$$

$1/[A]_t$



$$t_{1/2} = \frac{1}{k_2 [A]_0}$$



When,

$$t = t_{1/2}, [A]_t = [A]_0/2$$

For 2<sup>nd</sup> order reaction,

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + k_2 t_{1/2}$$

# Reaction Order at a glance

Order	Concentration profile	Half life, $t_{1/2}$	Straight line plot
0 <sup>th</sup>	$[A]_t = [A]_0 - k_0 t$	$t_{1/2} = \frac{[A]_0}{2k_0}$	$[A]_t = [A]_0 - k_0 t$
1 <sup>st</sup>	$[A]_t = [A]_0 e^{-k_1 t}$	$t_{1/2} = \frac{\ln 2}{k_1}$	$\ln[A]_t = \ln[A]_0 - k_1 t$
2 <sup>nd</sup>	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t$	$t_{1/2} = \frac{1}{k_2 [A]_0}$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t$

0-2'  
for further → Integrate yourself =

# Poll Question-1

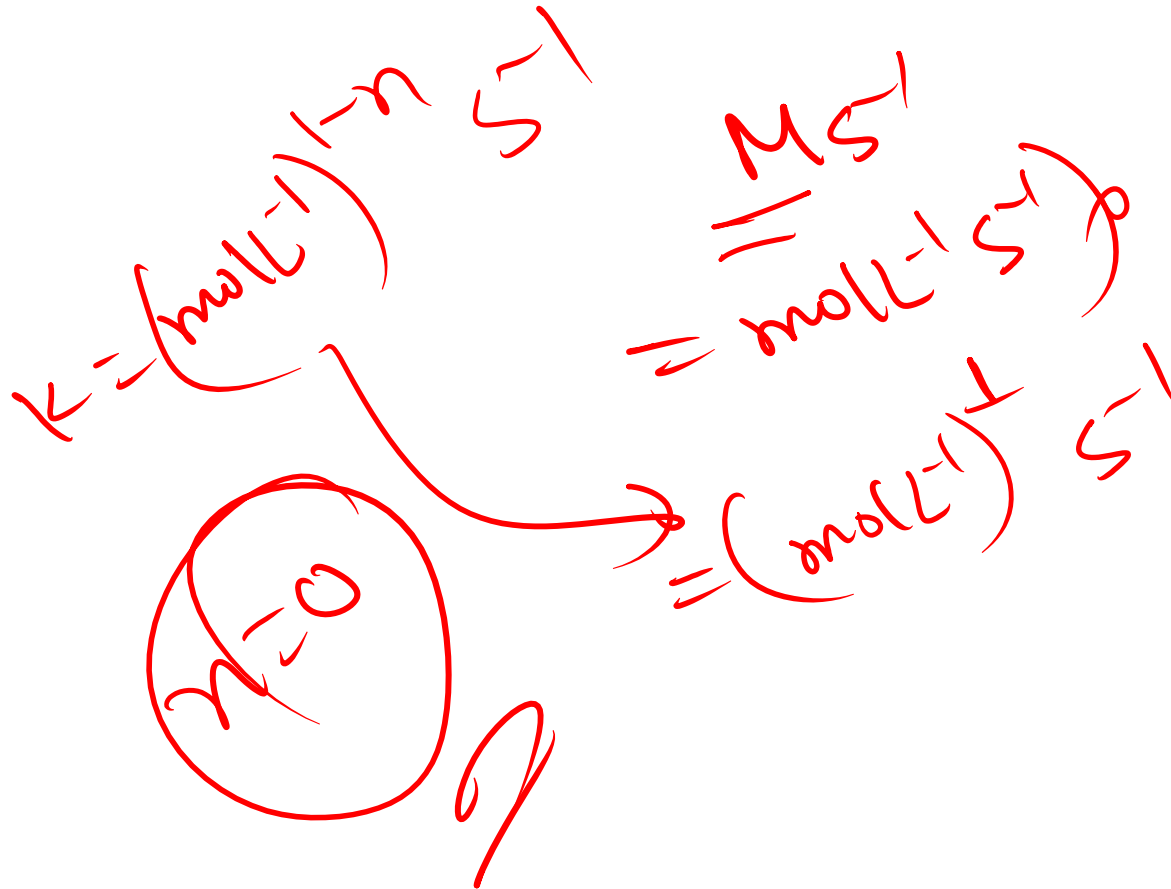
Rate constant for an irreversible reaction was found to be  $0.02 \text{ Ms}^{-1}$ .  
What is the order of the reaction?

(a) 1<sup>st</sup> order

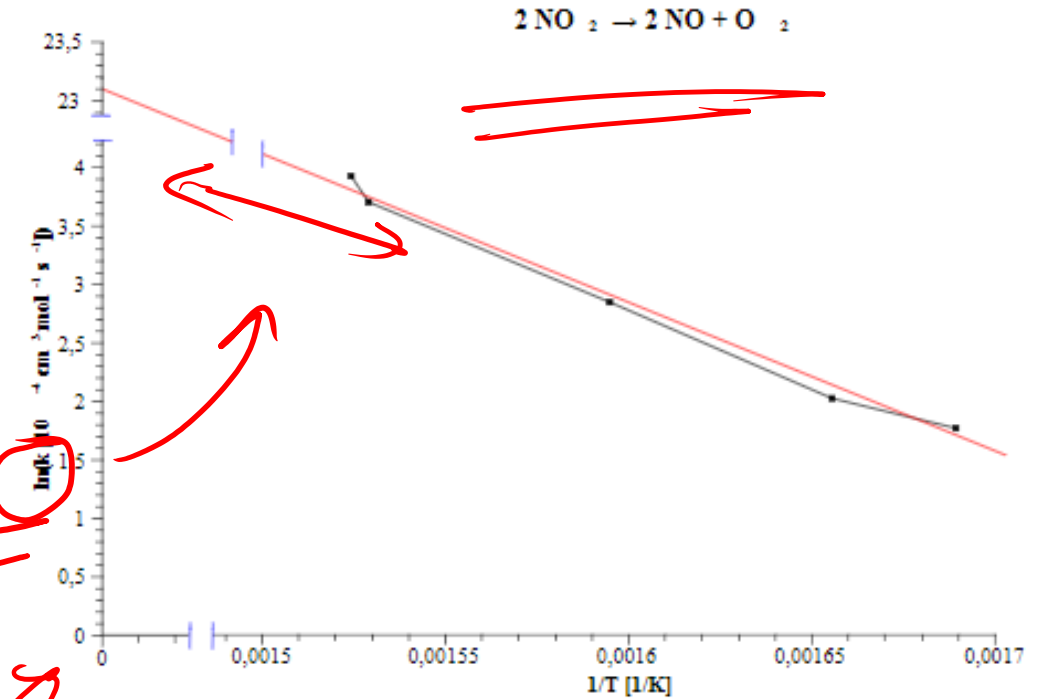
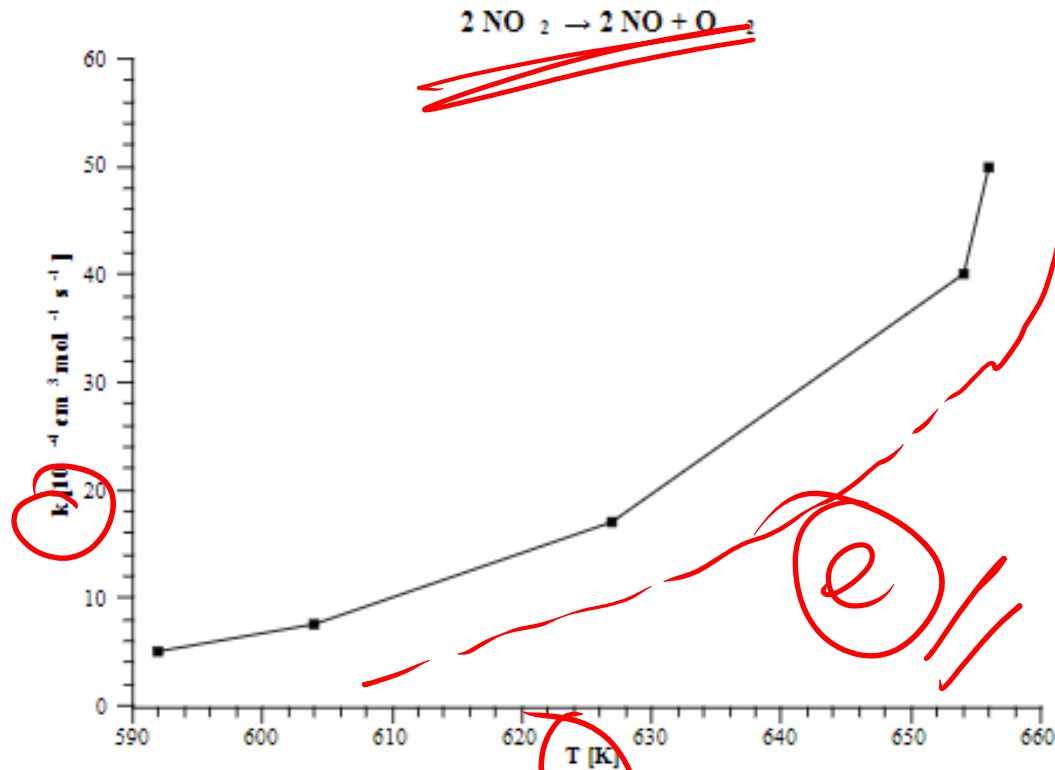
☒ (b) 0<sup>th</sup> order

(c) 2<sup>nd</sup> order

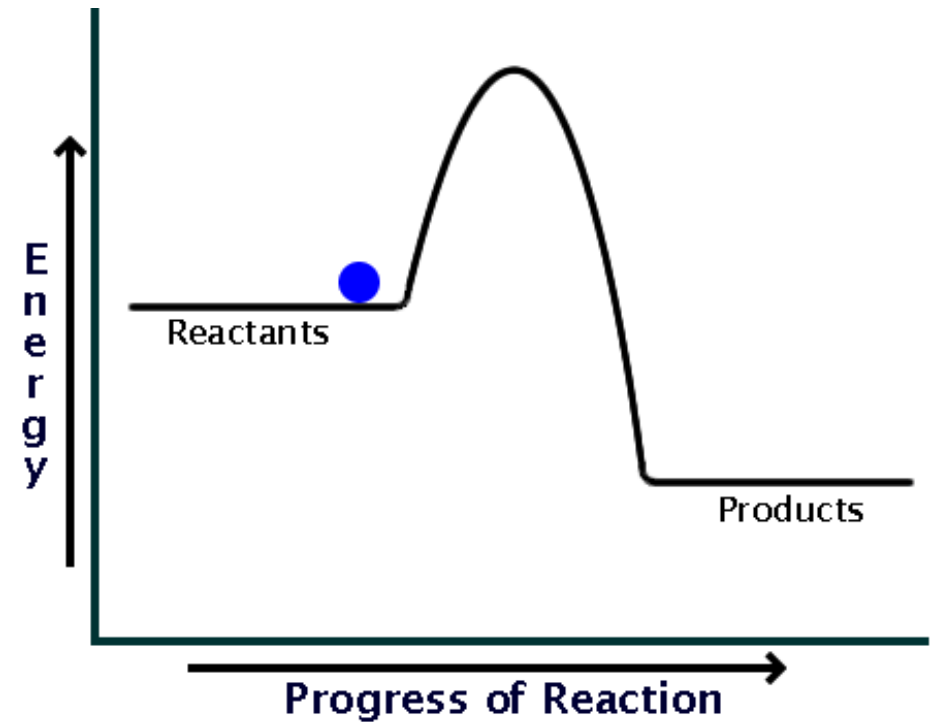
(d) 3<sup>rd</sup> order



# Effect of Temperature: Arrhenius Equation



$$k = Ae^{-\frac{E_a}{RT}}$$

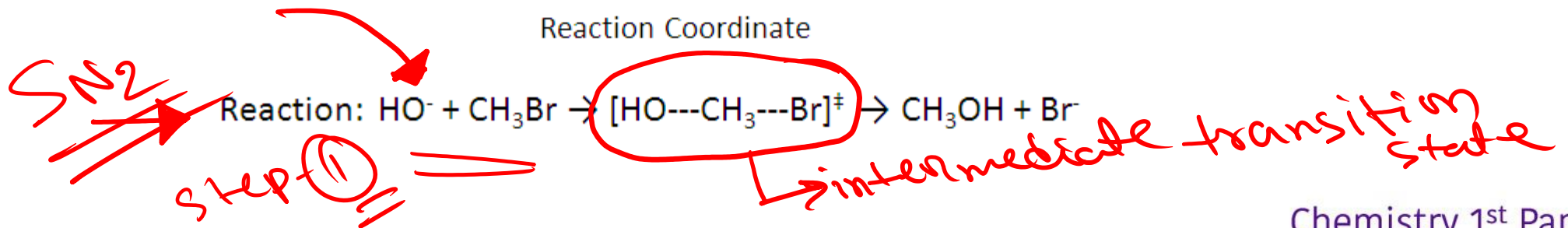
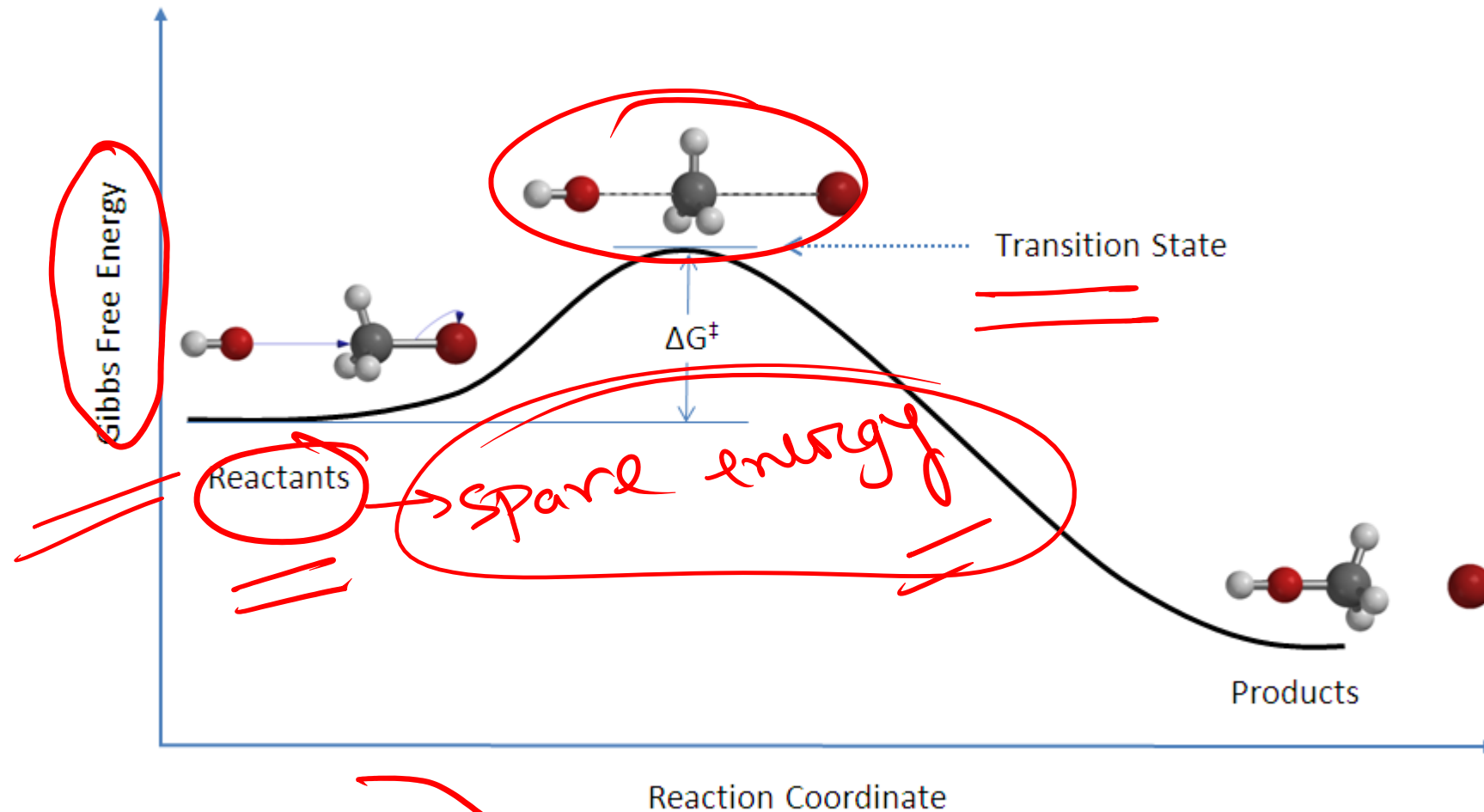


$$R_2 = A$$

i) Ea  
 ii) steric factor  
 iii) collision

Chemistry 1<sup>st</sup>

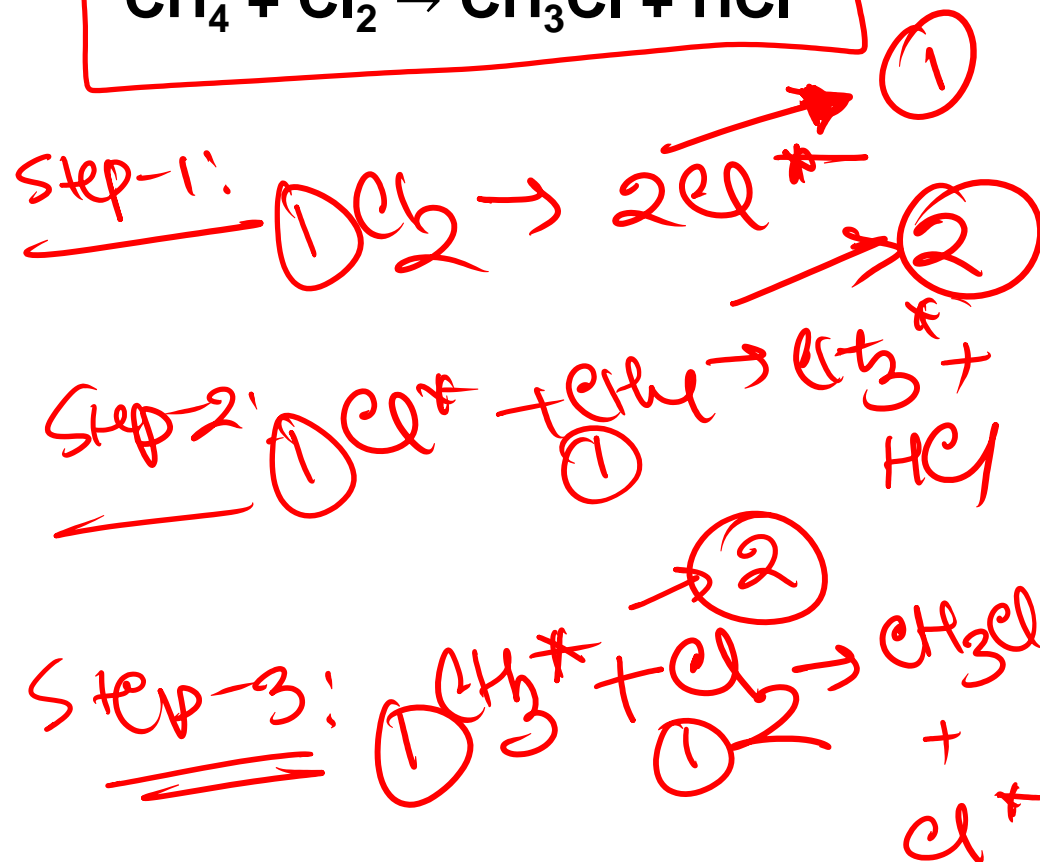
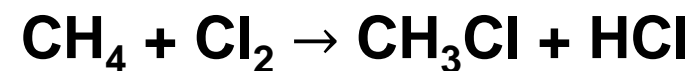
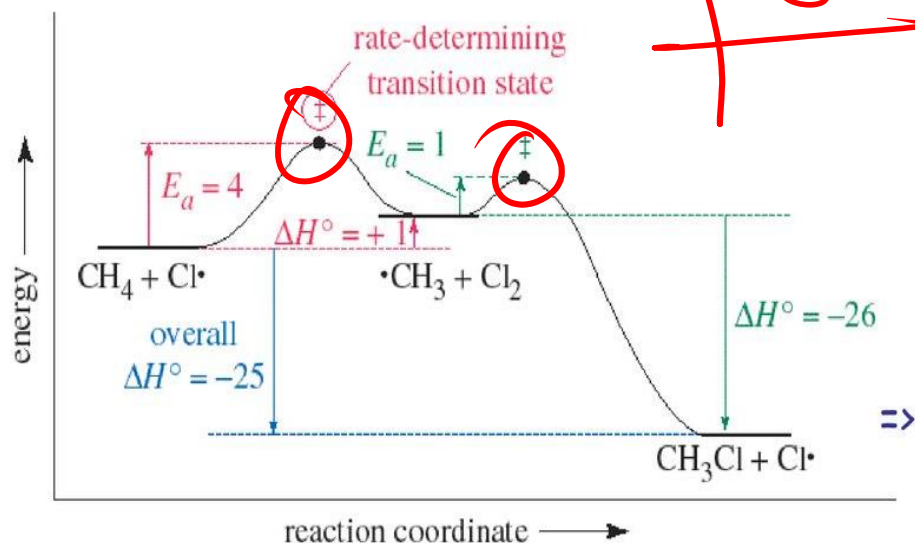
# Transition State Theory



# Transition State Theory

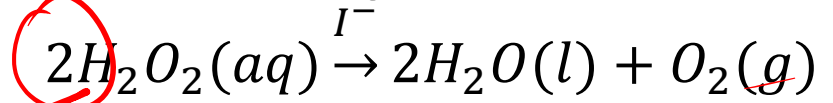
## Energy Diagram for a Two-Step Reaction

- Reactants → transition state → intermediate
- Intermediate → transition state → product



## Poll Question-2

The following reaction occurs in two steps. What is the molecularity of the reaction?



(a) One

(b) Two

(c) Three

☒ (d) Cannot be determined

if it would be single step  
↓  
2nd step not given  
particular molecularity  
not for whole reaction

## Problem-5

Activation energy for the gas phase dissociation reaction of  $\text{N}_2\text{O}_5$  is 103.5 Jmol<sup>-1</sup>. Calculate the ratio of rate constants at 0°C and 25°C.

BUET' 13-14

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$E_a = \underline{103.5 \text{ Jmol}^{-1}}$$

$$T_1 = 0^\circ\text{C} = 273\text{K}$$

$$T_2 = 25^\circ\text{C} = 298\text{K}$$

$$R = 8.314$$

$$\frac{k_2}{k_1} =$$



nt values of  
f the log k y  
n?

- (b)  $1.43 \text{ kJmol}^{-1}$

- $=$
- $2 = 8 \cdot 324$

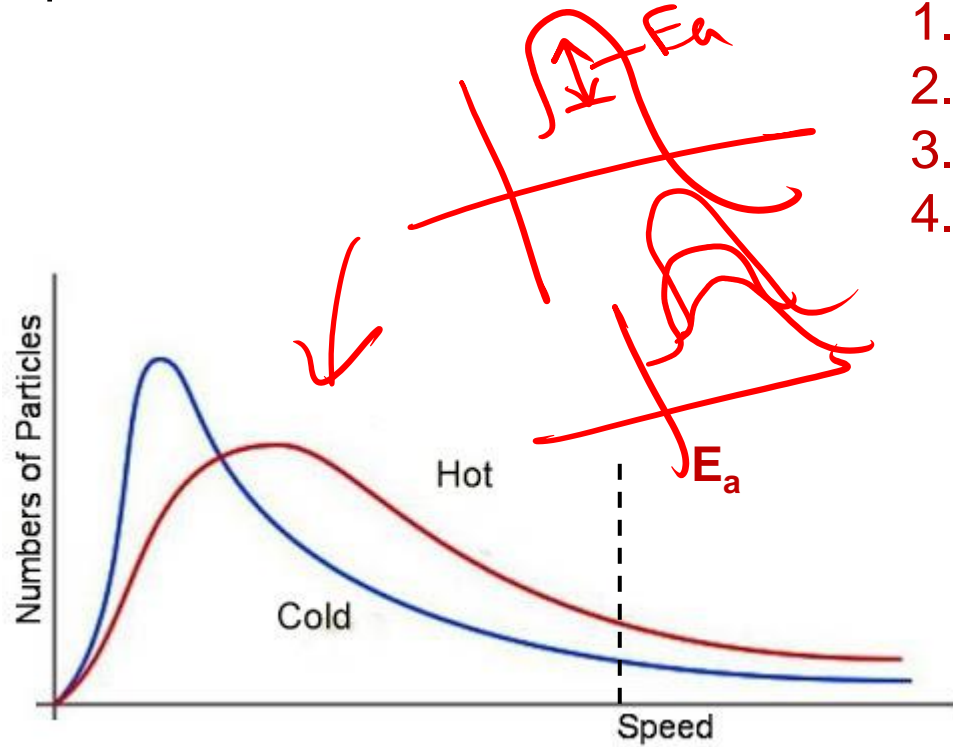
- (d)  $14.3 \text{ kJmol}^{-1}$

$$\therefore E_a = 75 \times R \times 2.303$$

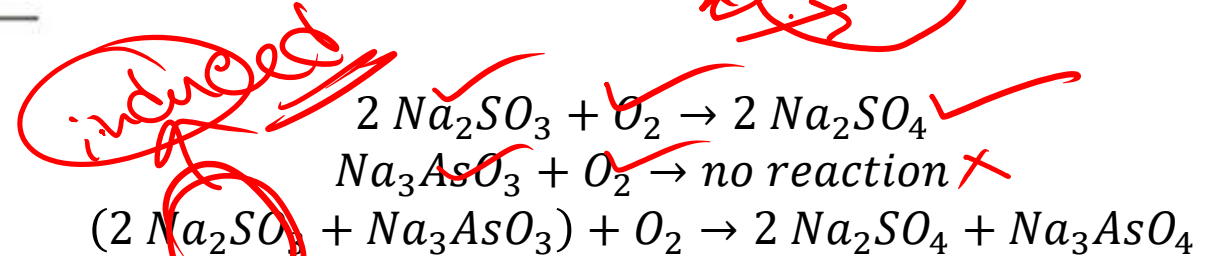
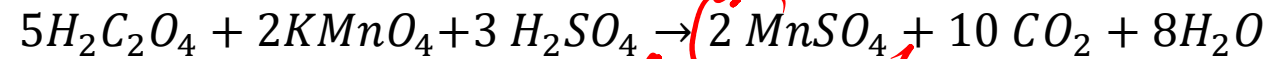
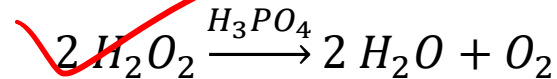
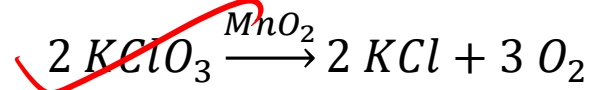


# Catalyst

Catalyst is a substance that alters the rate of any chemical process but doesn't change its chemical composition\* after the reaction.



1. Positive Catalyst  $\rightarrow E_a \downarrow$
2. Negative Catalyst  $\rightarrow E_a \uparrow$
3. Auto Catalyst  $\rightarrow$
4. Induced Catalyst  $\rightarrow$



# Thermochemistry

## Thermodynamics:

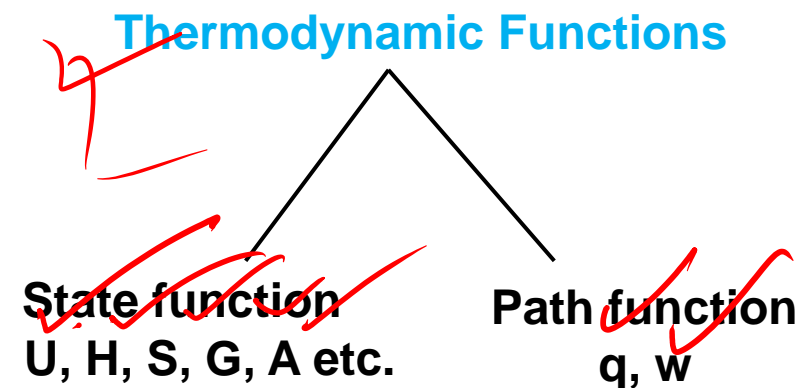
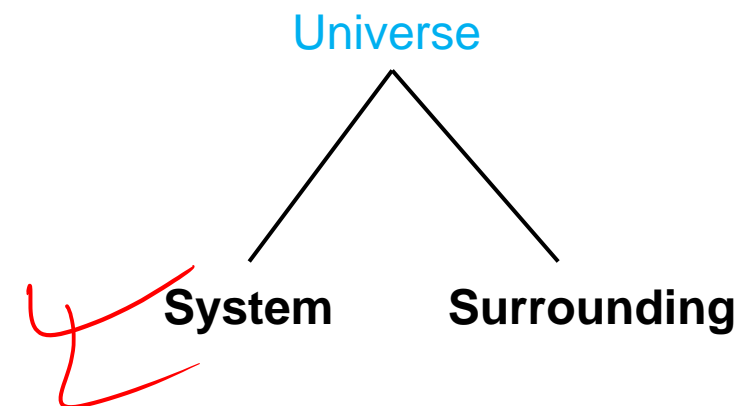
study of dynamics of "system" due to "heat". In other words, study of "interconversion" of "heat" with other forms of "energy"

## Thermochemistry:

Application of "thermodynamics" to "chemical systems"

## Description of a System:

- Pressure,  $P$
- Temperature,  $T$
- Amount,  $n$
- Volume,  $V$



# Laws of Thermodynamics

1. 0<sup>th</sup> Law



2. 1<sup>st</sup> Law

Change in Internal energy of a closed system is zero.

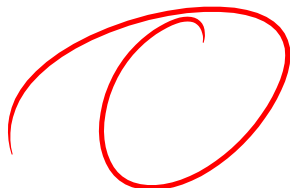
$$\Delta U_{\text{closed}} = 0$$

3. 2<sup>nd</sup> Law

Total entropy always increases in an irreversible process.  
Entropy change becomes zero at equilibrium, never decreases.

$$\Delta S_{\text{univ}} \geq 0$$

4. 3<sup>rd</sup> Law



# 1st Law of Thermodynamics

(Standard State)

Enthalpy,  $H = U + pV$

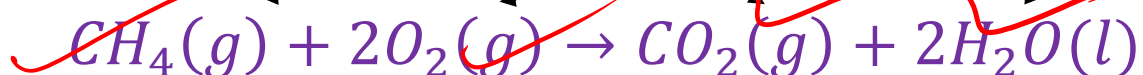
Change in enthalpy,  $\Delta H = q_p$

Change in internal energy,  $\Delta U = q_v$

Parameter	Standard State
Pressure	1 bar
Temperature	298 K
Matter	Pure solid/liquid

## Thermochemical Equation

Reactant and product at standard state



Change in standard enthalpy

$$\Delta H^\circ = -890.4 \text{ kJmol}^{-1}$$

$$\frac{890.4 \text{ kJ}}{1 \text{ mol}}$$

$$\frac{890.4 \text{ kJ}}{2 \text{ mol}}$$

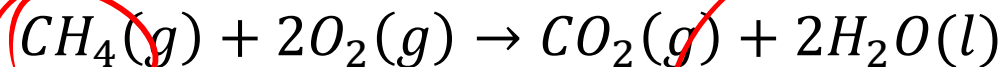
$$\frac{890.4 \text{ kJ}}{1 \text{ mol}}$$

$$\frac{890.4 \text{ kJ}}{2 \text{ mol}}$$

per mole

## Poll Question-4

What will be the energy released when 8.0 g of methane is completely burnt in excess oxygen at standard state?



$$\Delta H^\circ = -890.4 \text{ kJmol}^{-1}$$

(a) 445.2 kJ

(b) 445.2 J

(c) -445.2 kJ

(d) -445.2 J

$\Delta H = -ve$

# Standard Formation Enthalpy, $\Delta H_f^\circ$



Change in enthalpy when 1 mol of any compound is formed from its elements in standard state.



$$\Delta H_{\text{reaction}}^\circ = \Delta H_f^\circ (H_2O)$$

$$\text{If, } \Delta H_f^\circ (H_2) = 0$$

$$\Delta H_f^\circ (O_2) = 0$$

Def<sup>n</sup>:  
Standard formation  
enthalpy of elements is  
zero

## Problem-6

$$\Delta H = 804.8 \times 10^3 \text{ J}$$

1.0 mol methane produces 804.8 kJ of heat at 101.325 kPa constant pressure and 25°C temperature when ignited with enough oxygen. Calculate heat evolved at constant volume at this temperature and pressure.

$$\Delta H = \Delta U + P\Delta V$$

at const pressure  $\Delta H = \Delta U + P\Delta V$

$$\therefore PV = nRT \Rightarrow P\Delta V = \Delta nRT$$

$$\therefore \Delta V = \frac{\Delta nRT}{P}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\therefore \Delta U = \Delta H - \Delta nRT$$

$$\Delta U =$$



$$\Delta n = 1 - (1 + 2) = -2$$

$$\therefore P = 101.325 \text{ kPa} = 101325 \text{ Pa}$$

$$R = 8.314$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$



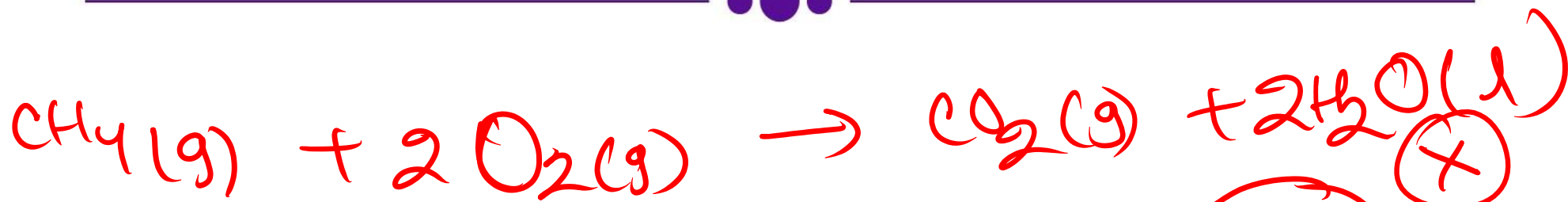
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Chemistry 1<sup>st</sup> Paper

Chapter 04 : Chemical Equilibrium

## Problem-6 (Continued)...

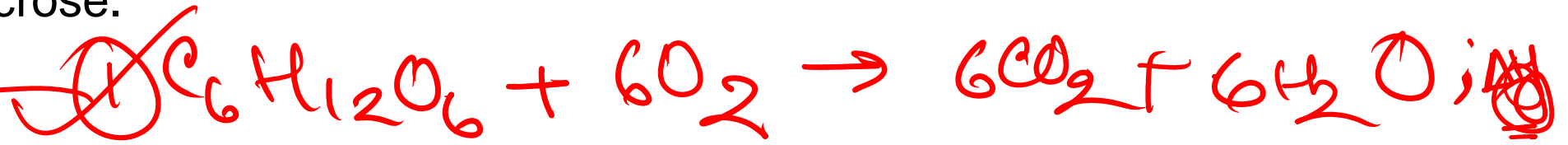


$$\Delta n = 1 - (1 + 2) = -2$$

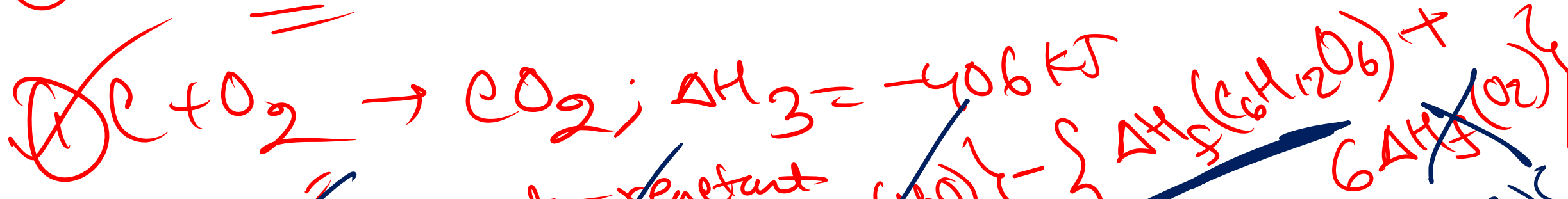
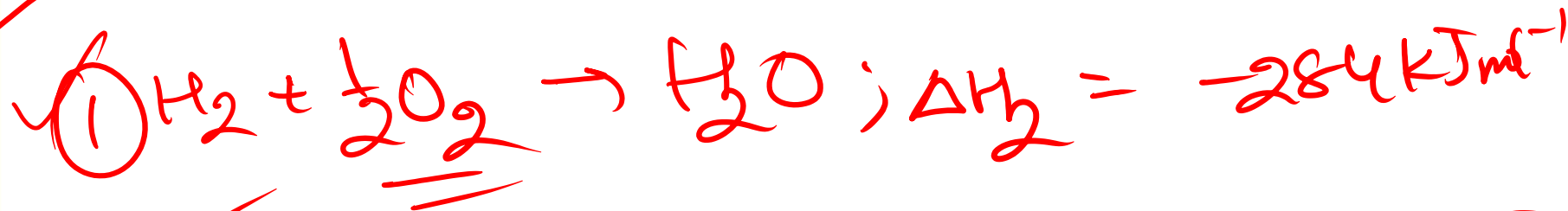
$$\begin{aligned} \Delta H &= \Delta U + P\Delta V \\ &= \Delta U + \Delta nRT \\ \therefore \Delta U &= \Delta H - \Delta nRT \end{aligned}$$

## Problem-07

Carbon, hydrogen and sucrose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) have standard heat of combustion values  $-406 \text{ kJmol}^{-1}$ ,  $-284 \text{ kJmol}^{-1}$  and  $-5638.82 \text{ kJmol}^{-1}$  respectively. Calculate standard formation enthalpy of sucrose.



$$\Delta H_1 = -5638.82 \text{ kJmol}^{-1}$$

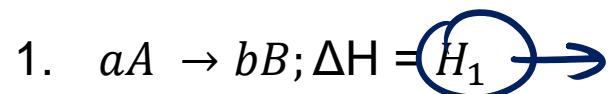


$$\Delta H_1 = \text{Product} - \text{reactant}$$

$$= \{ 6 \times \Delta H_f(\text{CO}_2) + 6 \times \Delta H_f(\text{H}_2\text{O}) \} - \{ \Delta H_f(\text{C}_6\text{H}_{12}\text{O}_6) + 6 \Delta H_f(\text{O}_2) \}$$

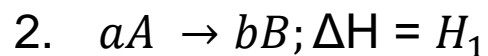
$$\Rightarrow \Delta H_f(\text{C}_6\text{H}_{12}\text{O}_6) = \{ 6 \times (-406) + 6 \times (-284) \} - \{ -5638.82 \} \text{ kJmol}^{-1}$$

# Properties of Thermochemical Equation

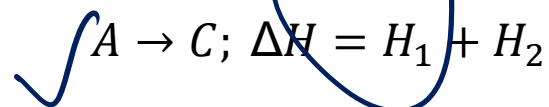
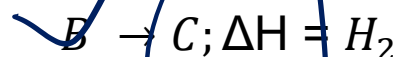


$$H_2 = -H_1$$

**Lavoisier- Laplace law**



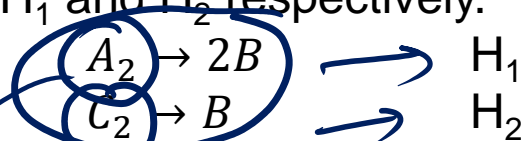
$$H_2 = nH_1$$



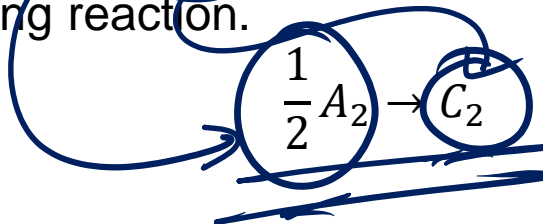
**Hess's law**

## Poll Question-5

Enthalpy of the following two reactions are  $H_1$  and  $H_2$  respectively.



Find the reaction enthalpy of the following reaction.



(a)  $H_1 - \frac{H_2}{2}$

(b)  $H_2 - \frac{H_1}{2}$

☒ (c)  $\frac{H_1}{2} - H_2$

(d)  $H_1 - H_2$

$$\textcircled{+} \frac{1}{2} \Delta H_1 - \Delta H_2$$

## Problem-08

Calculate Lattice enthalpy of  $\text{CaCl}_2$  from the given data-

(a) Heat of sublimation of Ca is  $H_{\text{sub}}$

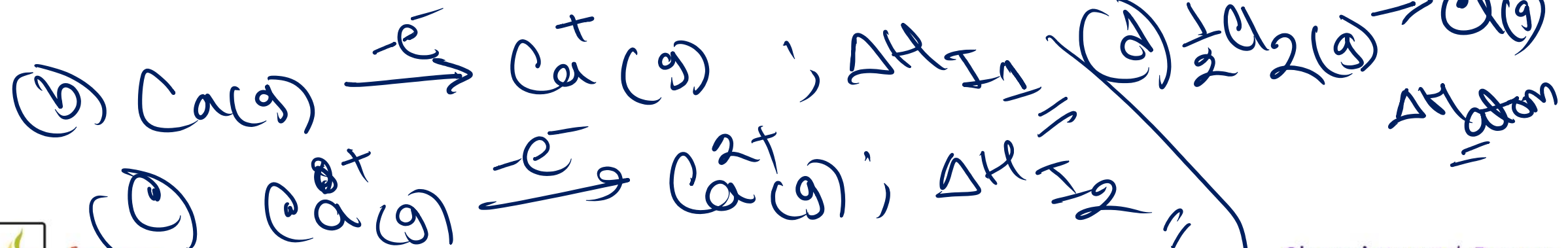
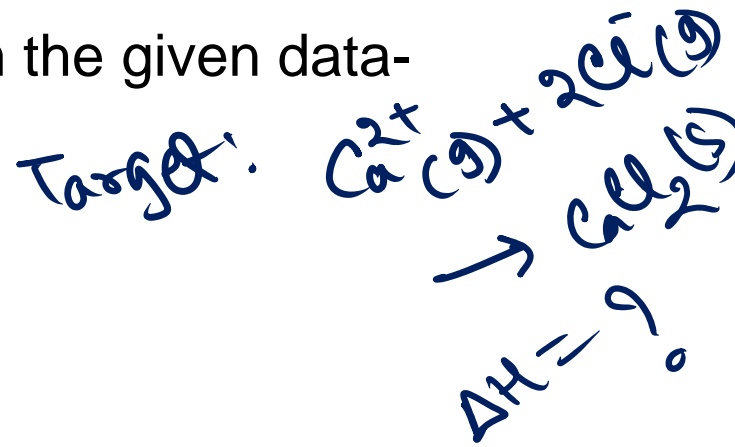
(b) 1<sup>st</sup> ionization energy of Ca is  $I_1$

(c) 2<sup>nd</sup> ionization energy of Ca is  $I_2$

(d) Heat of atomization of chlorine is  $H_{\text{atom}}$

(e) Electron affinity of chlorine is EA

(f) Heat of formation of  $\text{CaCl}_2$  is  $H_f$



## Problem-08 (Continued)...

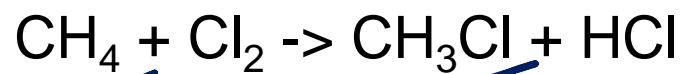


$\Delta H \underline{\underline{f}}$



## Problem-09

Calculate heat of the following reaction using the bond dissociation energy data given-

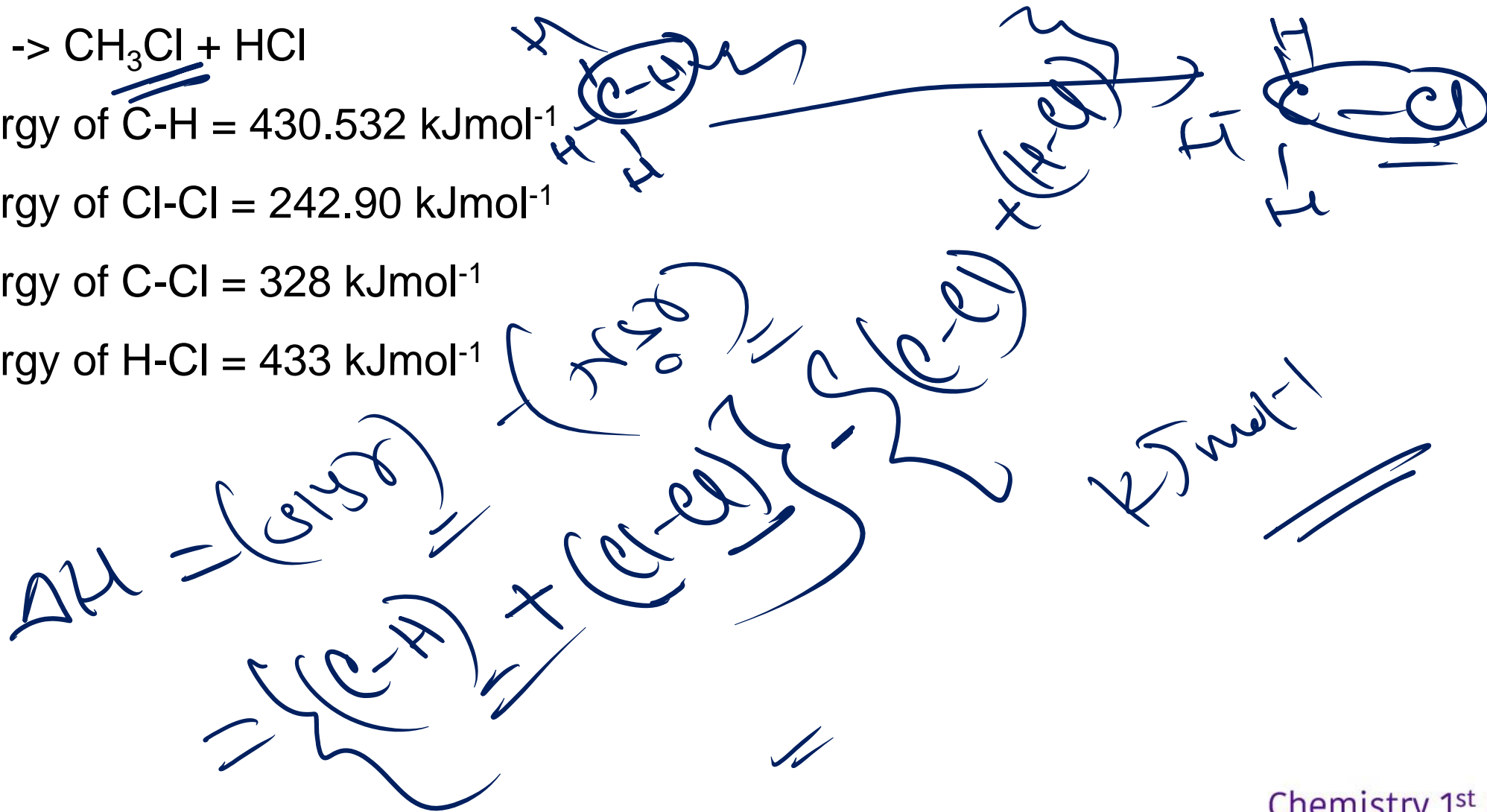


Bond energy of C-H =  $430.532 \text{ kJmol}^{-1}$

Bond energy of Cl-Cl =  $242.90 \text{ kJmol}^{-1}$

Bond energy of C-Cl =  $328 \text{ kJmol}^{-1}$

Bond energy of H-Cl =  $433 \text{ kJmol}^{-1}$



# 2nd Law of Thermodynamics

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$  is negative; spontaneous

$\Delta G$  is positive; non-spontaneous

$\Delta G = 0$ ; equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

At equilibrium,  $\Delta G=0$ ,  $Q = K$

$$\Delta G^0 = -RT \ln K$$

reading

$\Delta H$	$\Delta S$	$\Delta G$	example
+	+	- at high T	$\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$
-	-	- at low T	$\text{H}_2\text{O (g)} \rightarrow \text{H}_2\text{O (l)}$
+	-	Always +	$2\text{O}_3 \text{ (g)} \rightarrow 3\text{O}_2 \text{ (g)}$
-	+	Always -	$\text{NaOH(s)} \rightarrow \text{Na}^{\text{+}}\text{(aq)} + \text{OH}^{\text{-}}\text{(aq)}$

## Problem-10

Calculate the equilibrium constant for the decomposition reaction of water at 25°C.



Standard free energy of element is zero and  $\Delta G_f^0(H_2O) = 237.2 \text{ kJ/mol}$

$$\Delta G^0 = 2 \times \Delta G_f^0(H_2) + \Delta G_f^0(O_2) - 2 \times \Delta G_f^0(H_2O)$$

$$\Delta G^0 = 2 \times 0 + 0 - 2 \times 237.2$$

$$\Delta G^0 = -474.4 \text{ kJ/mol}$$

$$\Delta G^0 = -RT \ln K$$

$$\ln K = \frac{-\Delta G^0}{RT}$$

$$K = e^{\frac{-\Delta G^0}{RT}}$$

$$K = e^{\frac{-(-474.4)}{8.314 \times 298}}$$

$$K = e^{\frac{474.4}{2478.572}}$$

$$K = e^{1.913}$$

$$K = 6.75$$

লেগে থাকো সৎ ভাবে,  
স্বপ্ন জয় তোমারই হবে।